



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ :
C08F 10/02, 2/42, 2/34, 4/60, 4/24

A1

(11) International Publication Number: WO 00/58377

(43) International Publication Date: 5 October 2000 (05.10.00)

(21) International Application Number: PCT/US00/07573

(22) International Filing Date: 22 March 2000 (22.03.00)

(30) Priority Data:
60/127,247 31 March 1999 (31.03.99) US

(71) Applicant (for all designated States except US): CHEVRON
CHEMICAL COMPANY LLC [US/US]; 555 Market Street,
San Francisco, CA 94105 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): BYBEE, William, D.
[US/US]; 24309 Sunny Glen Drive, Huffman, TX 77336
(US). KRUTILEK, Mitchell, A. [US/US]; 1511 N. 25th,
Nederland, TX 77627 (US). KOMINEK, John, F. [US/US];
29006 Grace Lane, Highlands, TX 77562 (US).

(74) Agents: DEJONGHE, Thomas, G. et al.; Chevron Corporation,
Law Dept., P.O. Box 7141, San Francisco, CA 94120-7141
(US).

(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG,
BR, BY, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI,
GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE,
KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD,
MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD,
SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US,
UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS,
MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ,
BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE,
CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,
NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA,
GN, GW, ML, MR, NE, SN, TD, TG).

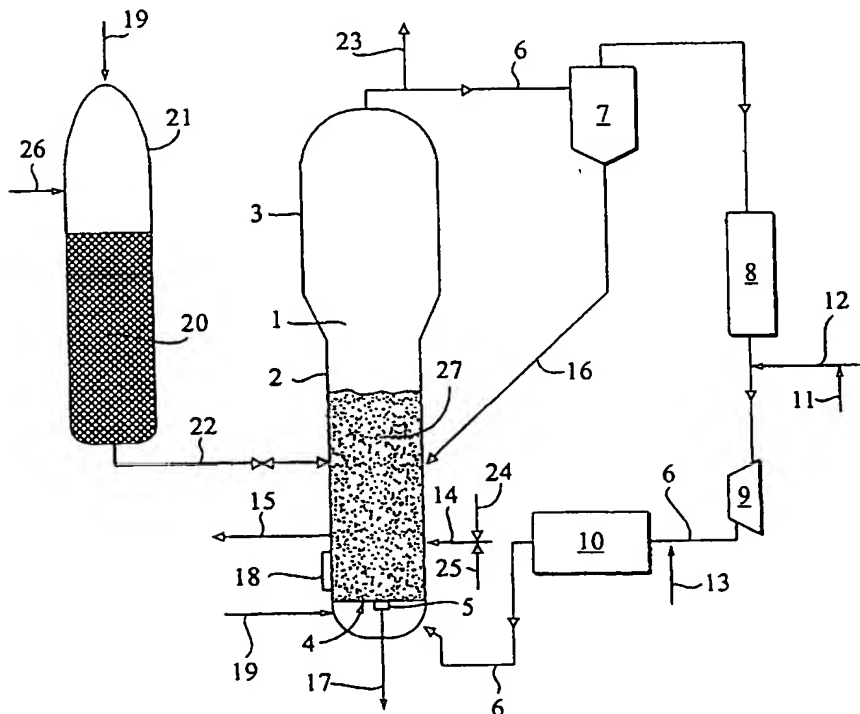
Published

With international search report.

(54) Title: PROCESS FOR CHANGING BETWEEN INCOMPATIBLE POLYMERIZATION CATALYSTS

(57) Abstract

An improved process for changing between two incompatible polymerization catalysts in a commercial scale olefins polymerization process. More particularly, the first polymerization is stopped and substantially all the polymer is removed, followed by rapid purging with nitrogen and start-up with a seedbed of high melting polymer.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

1 **PROCESS FOR CHANGING BETWEEN**
2 **INCOMPATIBLE POLYMERIZATION CATALYSTS**

3
4 **FIELD OF INVENTION**

5 The process of the invention is related to olefins polymerization and
6 the changeover between two incompatible polymerization catalysts. The
7 process involves emptying the reactor as part of this changeover. For
8 example, the first catalyst may be a Ziegler-Natta catalyst and the second
9 catalyst may be a metallocene catalyst.

10
11 **BACKGROUND AND RELEVANT REFERENCES**

12 From time to time during the production of olefin polymers in a
13 commercial reactor, it is necessary to convert from one type of catalyst
14 system producing polymers having certain properties and characteristics to
15 another catalyst system capable of producing polymers with somewhat
16 different properties and characteristics. However, this catalyst changeover is
17 often problematic and can be quite time-consuming.

18 For example Williams et al. in USP 4,460,755 teach that "when
19 converting from a Ziegler-type catalyst to a chromium-based catalyst, the
20 components of the Ziegler-Natta catalyst act as poisons for the chromium-
21 based catalyst, and that the chromium-based catalyst is ineffective in
22 promoting polymerization if it is introduced directly into the polymerization
23 reactor in the presence of the Ziegler-Natta catalyst. This is true even if a
24 large excess of the amount of chromium-based catalyst required to promote
25 polymerization is employed."

26 The Williams et al. patent teaches that "since direct conversion from
27 the use of a Ziegler-Natta catalyst to a chromium-based catalyst had proven
28 unsuccessful, such change of catalyst could heretofore be effected only "by
29 halting the polymerization reaction completely, emptying the reactor to rid it of
30 the original catalyst system, and then re-initiating polymerization with the new

1 catalyst system." They also teach that "in order to reinitiate polymerization
2 with the new catalyst, the recharged reactor first had to be purged to low
3 levels of oxygen and water, scavengers had to be employed to remove other
4 catalyst poisons, and prolonged induction periods had to be undergone after
5 such catalyst was introduced into the reactor before polymerization would
6 begin again. Consequently, such catalyst conversions were both time
7 consuming and costly, ordinarily requiring about 4 days or more of reactor
8 shutdown in a commercial operation before polymerization could once again
9 be re-initiated with the new catalyst." Williams et al., solve this transition
10 problem by using a hydroxyl-containing compound to interact with the Ziegler-
11 Natta catalyst before the Cr catalyst is introduced.

12 Similar problems exist when transitioning from Ziegler-Natta catalysts
13 to metallocene catalysts. In part this is because trying to operate
14 incompatible catalysts together leads to polymers with unacceptable
15 performance properties. For example, in making a polyethylene with a MI of
16 1.0, Ziegler-Natta catalysts require operating at high hydrogen concentrations
17 (about 6 mole% in the reactor) while metallocene catalysts must be operated
18 at low hydrogen concentrations (about 500 ppm). If the Ziegler-Natta
19 catalysts are operated at low hydrogen, they produce very high molecular
20 weight (MW) polymers. If the metallocene catalysts are operated at high
21 hydrogen concentrations they produce low molecular weight polymers.
22 Combining the two catalysts and operating at 500 ppm leads to a polymer
23 that contains ultra-high MW chains and hard particles. Processing this
24 polymer mix results in polyethylene films containing gels. The operating
25 conditions for the two catalyst systems are incompatible. Similarly, the
26 comonomer incorporation or uptake rates for the two catalyst systems are
27 very different. The Ziegler-Natta catalyst requires a much higher
28 concentration of comonomer in the feed to get the same degree of
29 incorporation in the polymer chains. At conditions useful for the Ziegler-Natta
30 catalyst, the metallocene catalyst produces very low-density polymer with

1 lower sintering temperature, which may cause sheeting in the bed. Thus it is
2 necessary to avoid the presence of both an active Ziegler-Natta catalyst and
3 an active metallocene catalyst during polymerization.

4 Agapiou et al. have patented a process for transitioning from one
5 incompatible catalyst to another. (See USP 5,442,019; 5,672,665; 5,753,786
6 and 5,747,612 which are incorporated herein by reference in their entirety.)
7 The process comprises the steps of: a) discontinuing the introduction of one
8 of the incompatible catalysts or catalyst systems into a reactor; b) introducing
9 an irreversible catalyst killer; and c) introducing into the reactor a second
10 catalyst or catalyst system incompatible with the first catalyst system. In one
11 embodiment the transition is between a traditional Ziegler-Natta type catalyst
12 system and a metallocene-type catalyst.

13 Although the Agapiou et al. method has some advantages, it also has
14 some disadvantages. For example, having the polymer product from the first
15 catalyst present during the transition results in product made from both
16 catalysts; this mixture may have less than optimum polymer properties (e.g.,
17 MWD, density, etc.). Also, the first catalyst must be killed by titration. Too
18 much kill agent will inactivate the second catalyst; too little will not meet the
19 process objective.

20 A serious disadvantage for the Agapiou et al. process lies in the fact
21 that an overly active metallocene catalyst can generate hot spots and polymer
22 sheets on startup, if the polymer bed is composed of LLDPE. Another
23 disadvantage is that any reactor chunks or sheets that have formed and
24 adhered to the reactor wall during operation of the first catalyst cannot be
25 removed during the catalyst change, since the reactor is not opened. With
26 the typically more active metallocene catalysts, failure to clean the grid and
27 reactor walls 1-2 meters above the grid often leads to problems. These
28 include faster grid plate and polymer withdrawal line plugging and wall fouling.

29 Borealis in WO 9732905 also teaches a method for transitioning
30 between two different catalysts in olefins polymerizations. The method

1 comprises: (a) discontinuing the feed of the first catalyst into the
2 polymerization reactor; and (b) introducing the second catalyst into the
3 reactor. The transitioning is performed between a chromium-based catalyst
4 and a metallocene catalyst. It is taught that the transition may be performed
5 rapidly without emptying the reactor. The reaction may be stopped and the
6 first catalyst deactivated, or a "flying" transition may be performed by stopping
7 the feed of the first catalyst, adjusting the reactor conditions and starting the
8 feed of the second catalyst.

9 None of the above patents are concerned with ways to shorten the
10 turnaround time for catalyst transitions where the reaction is stopped and
11 polymer, along with catalyst, are removed from the reactor.

12

13 SUMMARY OF THE INVENTION

14 In one embodiment the invention is an improved process for changing
15 between two incompatible polymerization catalysts in a commercial-scale
16 olefins polymerization process. The invention comprises: polymerizing olefins
17 with a first polymerization catalyst; stopping the polymerization; removing
18 substantially all of the polymer from the reactor, preferably including
19 non-powder polymer chunks; rapidly purging with nitrogen; adding a seedbed
20 of polymer particulates to the reactor, and polymerizing olefins with a second
21 polymerization catalyst.

22 We have now found that, for reactors having easy dump means, it is
23 just as simple and time-efficient to dump the reactor contents as to use the
24 poisoning techniques of the prior art. By the term "easy dump means" is
25 meant a mechanism whereby the reactor contents can readily and quickly be
26 removed. One such system with an easy dump means is shown in Figure 1.
27 Here the reactor incorporates a fluidization grid plate with a central opening
28 for polymer removal. It is preferred that the reactor also include a man-way
29 that allows for inspection and cleanup of the grid plate. Preferably there is a
30 vessel, e.g., a silo, external to the reactor to store a high melting polymer

1 seedbed. Preferably, the vessel has a high enough pressure rating to allow
2 using a high pressure N₂ line to quickly transfer the seedbed polymer into the
3 reactor. The reactor system also includes a high-pressure nitrogen line to
4 allow for rapidly purging the reactor.

5 With this sort of reactor system, one can readily stop polymerization
6 and without the use of catalyst kill agents, rapidly remove the olefin and
7 polymer particulates containing catalyst. The gas circulation is stopped (i.e.,
8 the compressor is shut down) and the reactor is opened and inspected.

9 After the polymer bed is removed, the reactor is opened. The reactor
10 is then inspected for any strips or chunks on the ground and walls, which are
11 removed if present. No special care is needed while inspecting the reactor
12 since no poisons are present. The reactor is closed and a N₂ purge is then
13 performed to remove any oxygen. Having high pressure N₂ and large
14 diameter purge lines significantly speeds up this process.

15 A drying agent, such as triethyl aluminum (TEA), is generally added at
16 this point to dry the reactor.

17 Then a seedbed of high melting polymer particulates, also called a
18 startup bed, is rapidly added to the reactor. This high melting point polymer is
19 selected to eliminate sheeting and chunking of the polymer during start-up. It
20 minimizes the potential for overheating and melting when the catalyst lights
21 off. Compared to using a low melting polymer, the use of a high melting
22 polymer particulates allows the catalyst to be added more rapidly.

23 In a preferred embodiment the invention is utilized with a continuous
24 polymerization process to make polyethylene, more preferably linear low
25 density polyethylene (LLDPE). Although the process is generally described
26 and exemplified herein as pertaining to ethylene polymerizations, it should be
27 understood that this is merely illustrative, and the invention encompasses
28 polymerization of other olefin or combinations of olefins.

1 When making LLDPE, the high melting polymer is preferably high
2 density polyethylene (HDPE). HDPE has a higher melting point (i.e., higher
3 sintering temperature) than the LLDPE.

4 After the reactor is closed and a high melting polymer seedbed is
5 added, reaction gases such as monomer, comonomer, and hydrogen, are
6 then added and circulated. Polymerization is initiated by feeding the second
7 catalyst and adjusting polymerization temperatures and pressures. An
8 important aspect of the present invention is to do the whole process rapidly
9 without fouling the reactor during startup with an overactive catalyst.

10 Preferably the down time is less than 3 days, more preferably less than
11 2 days.

12 In one preferred embodiment, the invention further comprises a
13 transition between comonomers. For example, a transition between a non-
14 polar and a polar comonomer coincides with the catalyst changeover.

15 In a preferred embodiment the invention is a process for changing
16 between two incompatible catalysts, a first catalyst and a second catalyst,
17 during olefins polymerization, said process comprising:

- 18 (a) operating an olefins polymerization plant which comprises a
19 reactor system having a reactor, means for easy polymer removal
20 and a means for polymer introduction, said plant utilizing a first
21 catalyst at a first set of polymerization conditions;
- 22 (b) stopping the polymerization;
- 23 (c) removing substantially all of the polymer from the reactor system;
- 24 (d) rapidly purging the reactor with nitrogen, preferably using a high
25 pressure purge line;
- 26 (e) drying the reactor;
- 27 (f) adding a seedbed of high melting polymer particulates to the
28 reactor;

- 1 (g) adding reaction gases comprising monomer, comonomer (if
2 desired), hydrogen, nitrogen, and an inert hydrocarbon (preferably
3 n-pentane, isopentane, n-hexane);
4 (h) adding said second polymerization catalyst to the reactor;
5 (i) polymerizing one or more olefins at a second set of polymerization
6 conditions.

7 Preferably, the polymerization is stopped without poisoning the catalyst
8 in the reactor. It is also preferred that any non-powder polymer chunks be
9 removed as part of step (c), above. Moreover, it is also preferred that the
10 process is completed in less than 3 days, more preferably in less than 2 days.
11 As will be discussed below, in one embodiment, the invention further
12 comprises a transition between comonomers, which coincides with the
13 catalyst change.

14 In step (g), preferably inert hydrocarbon and nitrogen are also included
15 in the gases. Also, comonomer is preferably included if co-polymerization
16 operation is desired.

17 Among other factors, the present invention is based on our finding that
18 catalyst changeovers can be accomplished without using catalyst kill agents
19 using a rapid changeover procedure in accordance with the procedure
20 described herein. Our time-saving process preferably uses high pressure
21 nitrogen introduced via one or more supply lines, and uses rapid purging,
22 preferably also in addition to using a seedbed of high melting polymer
23 particulates for controlling polymerization light-off. The process of the present
24 invention allows for rapid catalyst changeovers with short turnaround times,
25 even though polymer is removed from the reactor. The present process also
26 allows for reactor inspection and clean-up before polymerization with the
27 second catalyst begins.

28

BRIEF DESCRIPTION OF THE FIGURE

The Figure is a schematic of a reactor system useful in the present invention.

DETAILED DESCRIPTION OF THE INVENTION

In one broad aspect, the invention relates to changing between two incompatible catalysts in a commercial scale process operating in olefins polymerization plant. As used herein, "a commercial scale olefins polymerization process" is one that is primarily operated to produce polymer product for sale to customers, either internal or external customers. The process of the invention includes removing polymer from the reactor during the catalyst changeover.

The term "olefins" is used herein to preferably include ethylene; propylene; butene-1; hexenes such as 4-methylpentene-1 and hexene-1; octene-1; and decene-1. The olefins polymerization may be a homopolymerization, such as ethylene polymerization, or a co-polymerization, such as ethylene plus butene, propylene, or other olefins such as mentioned above.

In one especially preferred embodiment, the invention is a process for changing between two incompatible catalysts, a first catalyst and a second catalyst, during olefins polymerization, the process comprising:

- (a) operating an olefins polymerization plant which comprises a reactor system having a reactor, a grid plate, a means for easy polymer removal, and a means for polymer introduction, said plant utilizing said first catalyst at a first set of polymerization conditions;
- (b) stopping the polymerization without using a catalyst kill agent;
- (c) removing substantially all of the polymer from the reactor;
- (d) shutting down the compressor;
- (e) opening the reactor, and inspecting and removing non-powder chunks;

- 1 (f) rapidly purging the reactor with nitrogen;
- 2 (g) drying the reactor;
- 3 (h) adding a HDPE seedbed that is at least 40% of the weight of the
- 4 operational polymer bed to the reactor;
- 5 (i) adding reaction gases comprising monomer, comonomer,
- 6 hydrogen, nitrogen and an inert hydrocarbon;
- 7 (j) adding said second polymerization catalyst to the reactor;
- 8 (k) polymerizing one or more olefins at a second set of polymerization
- 9 conditions to produce a polyethylene product.

10 Preferably, the process is completed in less than 3 days, more
11 preferably in less than 2 days. The process may further comprise a transition
12 between comonomers.

13 As used herein, the term "incompatible catalyst" is used in the same
14 way as used in Agapiou et al., USP 5,753,786, bottom of Column 3.

15 "Incompatible catalysts" are those that satisfy one or more of the following:

16 (1) those catalysts that in each others presence reduce the activity of at least
17 one of the catalysts by greater than 50%; (2) those catalysts such that under
18 the same reactive conditions one of the catalysts produces polymers having a
19 molecular weight greater than two times higher than any other catalyst in the
20 system; and (3) those catalysts that differ in comonomer incorporation or
21 reactivity ratio under the same conditions by more than about 30%.

22 The process of this invention can be used in a gas phase, solution
23 phase, slurry or bulk phase polymerization process. A gas phase
24 polymerization process in a fluidized bed reactor is preferred, and may be
25 operated in condensed mode or in 100% gas phase.

26 In a typical continuous fluidized bed polymerization process for the
27 production of polymer from monomer, a gaseous stream comprising
28 monomer, with or without entrained liquids, is passed through a fluidized bed
29 reactor in the presence of a catalyst under reactive conditions. A polymer
30 product is withdrawn. Also withdrawn is a gas stream, which is recycled and

1 usually cooled, and together with additional monomer sufficient to replace the
2 monomer polymerized is returned to the reactor. In one embodiment, the
3 recycle gas stream is cooled to form a gas and a liquid phase mixture that is
4 then introduced into the reactor. For a detailed description of a gas phase
5 process, see U.S. Pat. Nos. 4,543,399; 4,588,790 and 5,668,228 which are
6 incorporated herein by reference.

7 While the preferred embodiment of the process of the invention is
8 directed to changing between a traditional Ziegler-Natta catalyst and a
9 metallocene catalyst, it is within the scope of this invention that the process of
10 the invention would apply to any change between incompatible catalysts. For
11 example, changing between a traditional Ziegler-Natta catalyst and a
12 chromium catalyst or changing between a chromium catalyst and a
13 metallocene catalyst or even change between a traditional Ziegler-Natta
14 titanium catalyst to a Ziegler-Natta vanadium catalyst. This invention
15 contemplates that the direction of changing between incompatible catalysts is
16 not limiting. However, it is preferred that the process of the invention involve
17 a change from or to a metallocene catalyst.

18 Traditional Ziegler-Natta catalysts typical in the art comprise a
19 transition metal halide, such as titanium or vanadium halide, and an
20 organometallic compound of a metal of Group 1, 2 or 3, typically
21 trialkylaluminum compounds. The latter serve as an activator for the
22 transition metal halide. Some Ziegler-Natta catalyst systems incorporate an
23 internal electron donor that is complexed to the alkyl aluminum or the
24 transition metal. The transition metal halide may be supported on a
25 magnesium halide or complexed thereto. This active Ziegler-Natta catalyst
26 may also be impregnated onto an inorganic support such as silica or alumina.
27 For more details on traditional Ziegler-Natta catalysts, see for example, U.S.
28 Pat. Nos. 3,687,920, 4,086,408, 4,376,191, 5,019,633, 4,482,687, 4,101,445,
29 4,560,671, 4,719,193, 4,755,495, 5,070,055, all of which are herein
30 incorporated by reference.

1 Metallocene catalysts, for example, are typically those bulky ligand
2 transition metal compounds derivable from the formula:



4 where L is a bulky ligand, A is an anionic ligand, B is a neutral donor ligand, p
5 is zero, one, two or three, M is a transition metal, and m and n are such that
6 the total ligand valency corresponds to the transition metal valency; m can be
7 one, two, three or four, and n can be zero or the valency state of the transition
8 metal minus m.

9 The ligands L and A may be bridged to each other, and the ligands L
10 and B may be bridged to each other, and if two ligands L and/or A are
11 present, they may be bridged. A may be a halide, an alkyl, an amide, or
12 phosphide, etc. B may be an oxygen donor such as tetrahydrofuran,
13 pyridine, thiophene, an alkene, or a diolefin.

14 The metallocene compound may be a full-sandwich compound having
15 two or more ligands L, which may be cyclopentadienyl ligands or
16 cyclopentadiene derived ligands, or half-sandwich compounds having one
17 ligand L, which is a cyclopentadienyl ligand or a cyclopentadiene derived
18 ligand.

19 The metallocene compounds contain a multiplicity of bonded atoms,
20 preferably carbon atoms, forming a group that can be cyclic. The bulky ligand
21 can be a cyclopentadienyl ligand or cyclopentadienyl derived ligand, which
22 can be mono- or poly-nuclear or any other ligand capable of η^5 bonding
23 to the transition metal. One or more bulky ligands may be π -bonded to the
24 transition metal atom. The transition metal atom may be a Group 4, 5 or 6
25 transition metal and/or a transition metal from the lanthanide and actinide
26 series. Other ligands may be bonded to the transition metal, such as those
27 indicated above. Non-limiting examples of metallocene catalysts and catalyst
28 systems are discussed in for example, U.S. Pat. Nos. 4,871,705, 4,937,299,
29 5,017,714, 5,120,867, 5,057,475, 5,096,867, 5,055,438, 5,227,440,
30 5,153,157, 5,198,401, 5,241,025, 4,530,914, 4,952,716, 5,064,802,

1 5,124,418, 4,808,561, 4,897,455, 5,470,993 and 5,616,664 all of which are
2 incorporated herein by reference.

3 In the preferred embodiment, the metallocene catalyst of this invention
4 is supported on support materials known in the art, for example, inorganic
5 oxides, like silica, alumina or magnesia or polymeric, such as polyethylene. It
6 is also contemplated by this invention that the metallocene catalyst of the
7 invention can be supported on a single support or separately supporting the
8 metallocene on one support and an activator on another support.

9 In the present invention, the first polymerization catalyst may be any
10 olefins polymerization catalyst including those described hereinabove.

11 The second polymerization catalyst may also be any olefins
12 polymerization catalyst including those described above, with the proviso that
13 the second catalyst be incompatible with the first catalyst.

14 The first and second catalysts may be added to the reactor system in
15 various ways. U.S. Patent No. 5,028,669 to Rowley et al., which is
16 incorporated herein by reference in its entirety, shows a variety of ways to
17 add catalyst that can be advantageously employed in this invention. Many
18 other ways known in the art for feeding particulates to a process stream will
19 also work with the present invention. In a preferred embodiment, the catalyst
20 is added to the reactor by a method described in U.S. Pat. No. 5,851,493 to
21 Lawson et al., which is incorporated herein by reference in its entirety. This
22 patent describes an injection system that includes a valve with at least one
23 cavity for receipt of particulate, and a sweep stream source for providing a
24 sweep stream to remove substantially all the particulate from the cavity of the
25 valve.

26 The invention utilizes a reactor system that includes a reactor, at least
27 one heat exchanger, at least one compressor and associated piping. In a
28 preferred embodiment, the reactor system further comprises a gas distribution
29 grid plate. By way of example, a reactor system useful in this invention is
30 shown schematically in FIG. 1. It includes a fluidized-bed reactor (1)

1 consisting of a vertical cylinder (2) surmounted by an expanded chamber,
2 also known as the disengaging section (3) and provided at its bottom part with
3 a fluidization grid (4). The grid has small openings for distributing the entering
4 reactant mixture and a larger opening (5) for polymer withdrawal. The reactor
5 system also comprises a line (6) for recycling the reaction mixture, which joins
6 the top of the fluidized-bed reactor to its bottom part. The recycling line (6)
7 includes, in succession in the direction of flow of the gaseous reaction
8 mixture, a cyclone (7), a first tube heat exchanger (8), a compressor (9) and a
9 second tube heat exchanger (10). Ethylene and hydrogen are added through
10 lines (11) and (12), respectively. Comonomer is added through line (13).

11 Line (14) makes it possible to feed the reactor (1) with solid catalyst.
12 Lines (24) and (25) are the feed lines for the different catalysts. Line (14)
13 needs to be clear of the first catalyst before it is used to feed the second
14 catalyst to the reactor.

15 While on-stream the produced polyolefin polymer particulates (27) are
16 discharged from the reactor (1) into line (15). During operation, fines are
17 reinjected into the reactor via line (16). Line (23) is a purge line for removing
18 gases from the reactor loop.

19 As part of the catalyst changeover, residual polymer particulates are
20 removed through grid withdrawal line (17). During operation, line (17) is
21 nitrogen purged. After the compressor (9) is shut off the blinds are rolled for
22 safety. Portal (18) is a man-way that may be opened to inspect the grid and
23 reactor walls. Non-powder polymer chunks can be manually removed during
24 inspection of the grid plate (4) after entry through the man-way (18). Residual
25 particulates can also be vacuumed out during this inspection. The high-
26 pressure nitrogen inlet line (19) is used to purge the reactor. High melting
27 polymer particulates (20), which are blanketed with nitrogen, from the
28 seedbed silo (21) are transferred into the reactor (1) through the seedbed
29 inlet line (22). Line (26) is used to fill the seedbed silo with polymer. Line
30 (27) represents the polymer in the bed.

1 The polymerization may be stopped in a variety of ways, such as
2 stopping catalyst feed, introducing a catalyst poison, or dropping the
3 temperature or pressure or monomer concentration below the minimums
4 necessary to sustain a polymerization reaction. It is preferred that the
5 polymerization be stopped by stopping the addition of the first catalyst.

6 After the polymerization is stopped, substantially all of the polymer is
7 removed from the reactor. First powder is removed via line (15) and then via
8 the grid opening (5). More preferably, before the compressor is turned off,
9 the bed is maintained above 150°F and olefins are purged through purge line
10 (23). It is preferred that the grid opening be located at the center of the grid
11 plate. It is small relative to the size of the grid plate, for example, about 4 to
12 6 inches compared to about 16 feet. By the term "substantially all the
13 polymer" is meant at least 90%, preferably at least 95%, more preferably at
14 least 98%, and most preferably at least 99.5 wt. % of the polymer.

15 One objective of the invention is to achieve a rapid turnaround time for
16 the catalyst changeover. The turnaround time is the time between when the
17 first catalyst is no longer added and the second catalyst lights off, i.e., begins
18 sustained olefins polymerization. It is desirable that this is done in less than
19 3.5 days, preferably in less than 3 days, and more preferably in less than
20 2 days.

21 As used herein, the term "rapid purge" or "rapidly purging" or the like
22 are intended to mean the quick dilution of catalyst poisons in a minimum time.
23 It is preferable to fill and empty the reactor several times to purge out any
24 residual poisons such as oxygen or water to very low levels preferably below
25 a few ppm.

26 This rapid purging can be accomplished, for example, by using large
27 diameter nitrogen lines and nozzles, or more preferably with high-pressure
28 nitrogen lines supplied at pressures greater than 50 psig, for example at
29 pressures of 100 psig and higher. Preferred pressures are between 125 and
30 400 psig, more preferably between about 150 and 350 psig, and most

1 preferably at a pressure of between about 300 and 350 psig. A rapid purge
2 which includes filling and emptying the reactor with nitrogen takes less than
3 an hour, preferably less than about 40 minutes, more preferably less than
4 about 30 minutes, and still more preferably less than about 20 minutes.
5 Rapidly purging the reactor with nitrogen significantly reduces the turnaround
6 time for the catalyst changeover. For the purposes of this application, rapid
7 purge means a nitrogen addition rate of at least 340 moles per hour and the
8 subsequent purging of at least that rate, more preferably at least 400 moles
9 per hour, still more preferably at least 500 moles per hour, and most
10 preferably at least 600 moles per hour. Temperature for purging operation is
11 preferably between 0°F and 150°F, more preferably between 40°F and 85°F.

12 For polymerization with Ziegler-Natta, metallocene or other water-
13 sensitive catalysts, the water level in the nitrogen purge gas should be below
14 1 ppm. Thus, depending on the water content in the reactor, a small amount
15 of a drying agent such as a trialkylaluminum compound may be added to
16 reduce the water level to less than 1 ppm. This drying or "pickling" of the
17 reactors and piping is common industry practice. Any of the well-known
18 drying agents may be used in this step. Preferred drying agents include
19 trialkyl aluminum compounds, such as trimethyl aluminum or more preferably
20 triethyl aluminum (TEA). This portion of the start-up procedure may be
21 accomplished by circulating the gases containing drying agent through the
22 empty bed for about one hour, followed by about three low-pressure N₂
23 purges to facilitate removal of TEA and water reaction products. The reactor
24 may then be repressured to 150 psig with N₂.

25 Preferably, a high melting seedbed is introduced to reduce bed
26 sheeting on startup after the LLDPE bed is withdrawn. Complete elimination
27 of bed sheeting and chunking on startup has been observed by using, for
28 example, a high melting polyethylene seedbed. It is important to use a high
29 melting polymer as the seedbed, since low-melting polymers can cause
30 problems on start-up. When polymerization is reinitiated, the temperature

1 may increase above the target temperature, due to the rapidly accelerating
2 reaction, and localized hot spots may be generated. This can soften or melt
3 the seedbed polymer and block the grid plate openings or polymer withdrawal
4 lines. For example, it has been found that using LLDPE as a seedbed
5 polymer often results in operational problems. We have found that using a
6 high melting polymer reduces bed sintering and prevents premature
7 shutdown. We have also found that using HDPE of a high MI, such as
8 greater than 6 MI, yields an initial product from the reactor that may be sold
9 as a molding resin.

10 It is not critical how the high melting polymer powder (also known as
11 particulates or fluff) is transferred into the reactor, although additional contact
12 with ambient air should be minimized. The powder can be transferred into the
13 reactor by suction or aspiration from a storage silo. Preferably, the silo is
14 appropriately pressure-rated and the polymer is transferred by blowing it into
15 the reactor using a high pressure nitrogen line.

16 The high melting polymer should not deactivate the polymerization
17 catalyst. Any polymer melting above the melt point of LLDPE (above about
18 220°F) meeting these criteria can be used. HDPE is an especially preferred
19 high melting polymer. For our purposes, HDPE having a density of
20 >0.940 g/cc may be used. HDPE with a density of >0.950 g/cc is preferred,
21 and MI above 6 is preferred for the HDPE selected for this use.

22 The amount of polymer seedbed should be sufficient to cover the fines
23 re-injection inlet line. This amount is at least 40% of the weight of the
24 operational polymer bed, more preferably at least 50%, and most preferably
25 about 60%. As used herein, the term "operational polymer bed" means the
26 amount of polymer particulates in the reactor when it is operated
27 commercially.

28 According to a preferred embodiment of the present invention, an
29 antistatic agent is introduced to the reactor after the seedbed, such as HDPE
30 seedbed is introduced, and prior to introducing the second catalyst, such as

1 the metallocene catalyst. We have found that such use of antistatic agent is
2 another factor that aids in successful transition and "light-off", including aiding
3 in avoiding of sheeting and/or chunking. Preferred amounts of antistat agent
4 are between about 1 ppm and 1000 ppm by weight based on polyethylene
5 production, more preferably between 5 ppm and 500 ppm, and most
6 preferably between 10 ppm and 80 ppm. Preferred antistat agents include
7 those types as described in USP 5,283,278, which is incorporated herein by
8 reference.

9 The feed or gas in the reactors is adjusted so that the catalyst will
10 produce a given product of a certain density and melt index. This generally
11 depends on how well a catalyst incorporates comonomer and its rate of
12 reaction with hydrogen. Typically, the gas composition also contains an
13 amount of hydrogen to control the melt index of the polymer to be produced.
14 In typical circumstances, the gas also contains an amount of dew point
15 increasing component with the balance of the gas composition made up of a
16 non-condensable inerts, for example, nitrogen.

17 Generally, the gas contains at least one alpha-olefin having from 2 to
18 20 carbon atoms, preferably 2-15 carbon atoms. Examples of alpha-olefins
19 include alpha-olefins of ethylene, propylene, butene-1, pentene-1,
20 4-methylpentene-1, hexene-1, octene-1, decene-1, and aromatic containing
21 olefins such as styrene. Other monomers can include dienes, norbornene,
22 acetylene, and polar vinyl compounds such as vinyl esters, vinyl ethers, vinyl
23 halides, vinyl amines and vinyl sulfides. Vinyl acetate is a preferred polar
24 comonomer. In the preferred embodiment, the gas composition contains
25 ethylene and at least one alpha-olefin having 3 to 15 carbon atoms. It is also
26 envisioned that a second, third or fourth comonomer may be added to make
27 terpolymers, tetramers and quintamers.

28 Although discussed herein in terms of catalyst changeovers, the
29 advantages of rapid polymerization transitions achieved through
30 polymerization shutdown and start-up can be applied to other polymerization

1 problems. Thus the advantages associated with seedbeds made of high
2 melting polymer particulates and the use of high-pressure nitrogen lines can
3 also be used for transitioning between comonomers. These comonomers
4 include non-polar comonomers such as alpha-olefins, i.e., transitions between
5 butene and hexene, and especially between polar comonomers containing
6 elements other than carbon and hydrogen, such oxygen, nitrogen, halogen or
7 sulfur atoms, such as vinyl acetate and vinyl chloride, or between polar and
8 non-polar comonomers. It is envisioned that the catalyst changeover process
9 of the invention will, in some instances, also include a transition between
10 comonomers.

11 Depending on the second catalyst to be introduced into the reactor, the
12 concentration of reactants, such as monomer, comonomer and hydrogen gas,
13 can be increased or decreased. In the preferred embodiment, the
14 concentrations of comonomer and hydrogen are decreased, particularly when
15 a metallocene catalyst is utilized as the second catalyst in the process of the
16 invention.

17 Typically, the reactant gas composition is diluted as above, for
18 example, by either pressure purging or flow purging, procedures well known
19 in the art. Once the reactant concentrations are sufficiently diluted to
20 accommodate the second catalyst and substantially all poisons are removed,
21 the next step in the invention is to introduce the second catalyst.

22 Once the bed is fluidized and the new gas composition is introduced
23 into the reactor, the second catalyst is introduced into the reactor under
24 reactive conditions.

25 To obtain a more complete understanding of the present invention, the
26 following examples illustrating certain aspects of the invention are set forth. It
27 should be understood, however, that the invention is not intended to be
28 limited in any way to the specific details of the following examples.

29

EXAMPLES

The following example and Table 1 illustrate the invention when making LLDPE in a gas phase reactor. Here the change is from a Ziegler-Natta catalyst to a metallocene catalyst. Example 1 uses an LLDPE seedbed (added by aspiration from a storage silo). It uses a conventional nitrogen supply line at 50 psig. In Example 2 of the invention, a high-pressure nitrogen purge system (at about 325 psig) is used with an HDPE seedbed, which is blown into the reactor using nitrogen pressure. The HDPE seedbed allows more rapid catalyst start-up since concerns about polymer sintering are reduced. The specifics for Example 2 are described in detail below. These two examples both include the same 21 steps.

1. Stop feeding the Ziegler-Natta catalyst.
2. Reduce the reactor pressure from about 325 to about 150 psig.
3. Draw down the polymer bed, thus also removing the bulk of the catalyst. Add nitrogen to displace the hydrocarbons.
4. Empty remaining polymer and catalyst from reactor through grid plate port.
5. Stop gas circulation (i.e., stop the compressor).
6. Close valves to block off feed lines and put blinds in place (for safety).
7. Open reactor and preferably inspect reactor, especially grid. Remove any sheets or chunks on grid or along walls, and ensure grid is good and clean.
8. Close reactor and remove blinds on feed lines.
9. Rapidly purge the reactor of oxygen using a high-pressure (about 325 psig) nitrogen (N₂) purge line, purge 3 times (3X) filling the reactor with N₂ to between 5-20 psig each time.
10. Start compressor.

- 1 11. Rapidly purge the reactor using a high pressure N₂ line several times.
2 The purge operations are continued (usually about seven times) until the
3 moisture level is constant. It typically stabilizes at a moisture reading of
4 about 5 ppm or less. With the use of a high-pressure nitrogen line, steps
5 9, 11 14 and 15 can be done rapidly.
- 6 12. Depending on the water content in the reactor, add a small amount of
7 triethyl aluminum (TEA) to reduce water level to <1 ppm.
- 8 13. Circulate gases through the empty bed.
- 9 14. Rapidly purge 3 times using high-pressure N₂ lines to facilitate removal of
10 TEA and water reaction products.
- 11 15. Repressure to 150 psi with N₂.
- 12 16. Test for leaks.
- 13 17. Drop pressure. In Example 1, the reactor pressure is dropped to 130
14 psig. In Example 2, the reactor pressure is dropped to 5-10 psig in order
15 to facilitate transferring the polymer powder with high-pressure nitrogen
16 from the seedbed silo.
- 17 18. Transfer the seedbed polymer into the reactor. The amount transferred
18 is equal to about 1/2 the weight of the operational bed. The transfer can
19 be done by various means such as by aspiration of polymer powder from
20 a nitrogen-blanketed storage silo, or preferably by blowing the powder
21 from a storage silo using nitrogen.
- 22 19. Make polymerization composition by adding feed and other gases, e.g.,
23 ethylene monomer, hexene or butene comonomer, and H₂, and then heat
24 reactor to 180°F. Optionally, an antistatic agent can be added in an
25 amount of 5 to 500 ppm by weight based on the polymer production rate.
- 26 20. Start feeding the metallocene catalyst; the reactor will light, i.e.,
27 polymerization will begin, within four to ten hours.

- 1 21. Adjust polymerization conditions to make product meeting LLDPE
- 2 polymer specifications.
- 3 Table 1 shows the approximate times for each step.

Table 1

COMMERCIAL SCALE PLANT CHANGEOVERS BETWEEN CATALYSTS					
Step	Task	Example 1	Example 1	Example 2	Example 2
		Task hr	Total hr	Task hr	Total hr
1	Stop First Catalyst	0.25	0.25	0.25	0.25
2	Vent Reactor to 150 psig	0.50	0.75	0.50	0.75
3	Draw down Bed	6.00	6.75	6.00	6.75
4	Empty bed through grid plate	1.50	8.25	1.50	8.25
5	Stop Compressor	0.25	8.50	0.25	8.50
6	Roll Blinds	3.50	12.00	3.50	12.00
7	Open and inspect reactor	3.00	15.00	3.00	15.00
8	Roll Blinds	3.50	18.50	3.50	18.50
9	3X purge w/N ₂ to remove O ₂ (5-20 psig)	3.00	21.50	1.75	20.25
10	Start Compressor	0.25	21.75	0.25	20.50
11	Multiple purges w/N ₂ until H ₂ O constant (5-40 psig)	7.00	28.75	3.50	24.00
12	Inject TEA if H ₂ O > 1 ppm	0.35	29.10	0.35	24.35
13	Circulate TEA in empty bed	1.00	30.10	1.00	25.35
14	Purge 3X w/N ₂ for TEA product removal (10-40 psig)	3.00	33.10	1.75	27.10
15	Add N ₂ to 150 psig	1.00	34.10	0.60	27.70
16	Leak test	1.00	35.10	1.00	28.70
17	Drop pressure**	0.50	35.60	0.80	29.50
18	Add seedbed*	7.00	42.60	1.00	30.50
19	Make composition, add antistat	4.00	46.60	4.00	34.50
20	Start second catalyst	12.00	58.60	6.00	40.50
21	Adjust conditions	5.00	63.60	5.00	45.50

- 4
- 5 ** Example 1 reactor pressure 130 psig, Example 2 reactor pressure 5-10
- 6 psig.
- 7 * Example 1 uses LLDPE via aspiration, Example 2 uses HDPE via nitrogen
- 8 blow-in.

1 As can be seen, the use of HDPE as the seedbed, transferring the
2 seedbed powder using pressurized nitrogen to blow it into the reactor and
3 purging using high-pressure nitrogen supply lines reduces the total
4 turnaround time for the changeover significantly.

5 While the invention has been described above in terms of preferred
6 embodiments, it is to be understood that variations and modifications may be
7 used as will be appreciated by those skilled in the art. Indeed, there are
8 many variations and modifications to the above embodiments which will be
9 readily evident to those skilled in the art, and which are to be considered
10 within the scope of the invention as defined by the following claims.

1 WHAT IS CLAIMED IS:

2

- 3 1. An improved process for changing between two incompatible
4 polymerization catalysts in a commercial scale olefins polymerization
5 process, comprising:
6 polymerizing olefins with a first polymerization catalyst; stopping the
7 polymerization; removing substantially all of the polymer from the
8 reactor; rapidly purging with nitrogen; adding a seedbed of polymer
9 particulates to the reactor, and polymerizing olefins with a second
10 polymerization catalyst.
- 11 2. A process in accordance with claim 1 wherein the process is
12 completed in less than 3 days.
- 13 3. A process in accordance with claim 1 wherein the process is
14 completed in less than 2 days.
- 15 4. A process in accordance with claim 1 wherein the polymerization is
16 stopped without poisoning the catalyst in the reactor.
- 17 5. A process in accordance with claim 1 wherein the polymer seedbed
18 comprises HDPE.
- 19 6. A process in accordance with claim 1 further comprising removing
20 non-powder polymer chunks.
- 21 7. A process in accordance with claim 1 wherein the olefins comprise
22 ethylene.
- 23 8. A process in accordance with claim 1 wherein the olefins comprise
24 ethylene and a comonomer selected from propylene, butene-1,
25 4-methylpentene-1, octene-1 or decene-1.
- 26 9. A process in accordance with claim 1 wherein the polymer produced is
27 polyethylene.
- 28 10. A process in accordance with claim 1 wherein the change in
29 polymerization catalysts is between a Ziegler-Natta catalyst and a
30 metallocene catalyst.

- 1 11. A process in accordance with claim 1 wherein the change in catalysts
2 is between a chromium-based catalyst and a metallocene catalyst.
- 3 12. A process in accordance with claim 1 wherein after the polymerization
4 is stopped, at least 95% of the polymer is removed from the reactor.
- 5 13. A process for changing between two incompatible catalysts, a first
6 catalyst and a second catalyst, during olefins polymerization, said
7 process comprising:
- 8 (a) operating an olefins polymerization plant which comprises a
9 reactor system having a reactor, means for easy polymer removal
10 and a means for polymer introduction, said plant utilizing a first
11 catalyst at a first set of polymerization conditions;
- 12 (b) stopping the polymerization;
- 13 (c) removing substantially all of the polymer from the reactor system;
- 14 (d) rapidly purging the reactor with nitrogen;
- 15 (e) drying the reactor;
- 16 (f) adding a seedbed of high melting polymer particulates to the
17 reactor;
- 18 (g) adding reaction gases comprising monomer, comonomer,
19 hydrogen, nitrogen, and an inert hydrocarbon;
- 20 (h) adding said second polymerization catalyst to the reactor;
- 21 (i) polymerizing one or more olefins at a second set of
22 polymerization conditions.
- 23 14. A process in accordance with claim 13 wherein the process is
24 completed in less than 3 days.
- 25 15. A process in accordance with claim 13 wherein the process is
26 completed in less than 2 days.
- 27 16. A process in accordance with claim 13 wherein the polymerization is
28 stopped without poisoning the catalyst in the reactor.
- 29 17. A process in accordance with claim 13 wherein the polymer seedbed
30 comprises HDPE.

- 1 18. A process in accordance with claim 13 further comprising removing
2 non-powder polymer chunks.
- 3 19. A process for changing between two incompatible catalysts, a first
4 catalyst and a second catalyst, during olefins polymerization, the
5 process comprising:
- 6 (a) operating an olefins polymerization plant which comprises a
7 reactor system having a reactor, a grid plate, a means for easy
8 polymer removal, and a means for polymer introduction, said
9 plant utilizing said first catalyst at a first set of polymerization
10 conditions;
- 11 (b) stopping the polymerization without using a catalyst kill agent;
- 12 (c) removing substantially all of the polymer from the reactor;
- 13 (d) shutting down the compressor;
- 14 (e) opening the reactor, and inspecting and removing non-powder
15 chunks;
- 16 (f) rapidly purging the reactor with nitrogen;
- 17 (g) drying the reactor;
- 18 (h) adding a HDPE seedbed that is at least 40% of the weight of the
19 operational polymer bed to the reactor;
- 20 (i) adding reaction gases comprising monomer, comonomer,
21 hydrogen, nitrogen, and an inert hydrocarbon;
- 22 (j) adding said second polymerization catalyst to the reactor;
- 23 (k) polymerizing one or more olefins at a second set of
24 polymerization conditions to produce a polyethylene product.
- 25 20. A process in accordance with claim 19 wherein the process is
26 completed in less than 3 days.
- 27 21. A process in accordance with claim 19 wherein the process is
28 completed in less than 2 days.
- 29 22. The process of claims 1 or 13 or 19 wherein the process further
30 comprises a transition between comonomers.

1/1

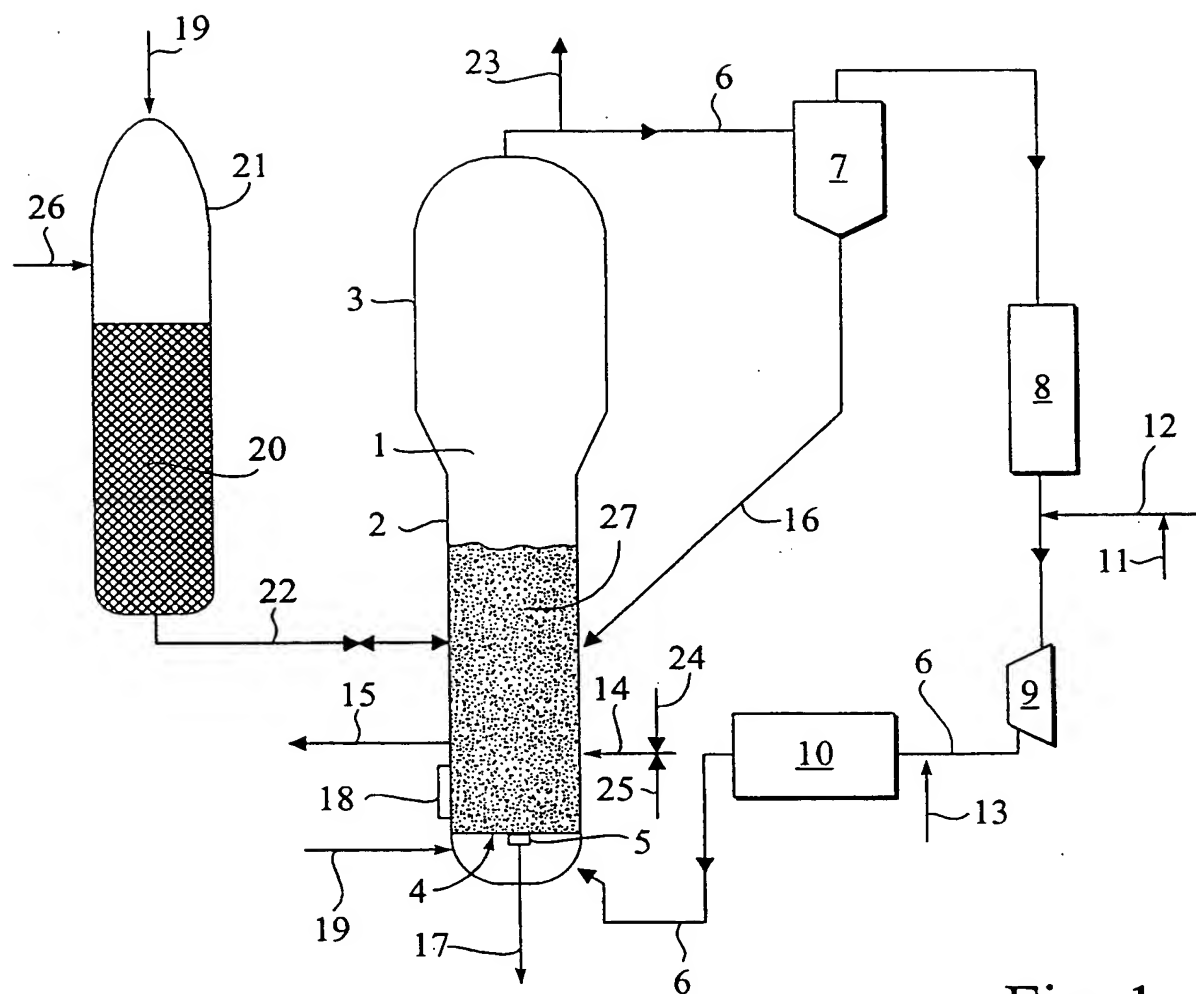


Fig. 1

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 00/07573

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08F10/02 C08F2/42 C08F2/34 C08F4/60 C08F4/24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	W0 96 39450 A (EXXON CHEMICAL PATENTS INC) 12 December 1996 (1996-12-12) page 17, line 8 - line 15; claims; examples page 18, line 4 - line 13 page 21, line 1 - line 14 page 26, line 9 - line 15 claims	1-22
A	W0 97 32905 A (BOREALIS AS ;ALMQUIST VIDAR (NO); AASTAD TONE (NO); MELAAEN INGRID) 12 September 1997 (1997-09-12) cited in the application claims; examples --- -/--	1-22

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

3 July 2000

Date of mailing of the international search report

18/07/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Kaumann, E

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/07573

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 442 019 A (AGAPIOU AGAPIOS K ET AL) 15 August 1995 (1995-08-15) cited in the application the whole document ---	1-22
A	DE 42 41 530 A (BUNA AG) 16 June 1994 (1994-06-16) claim ---	1-22
A	US 5 763 543 A (GRIFFIN JOHN ROBERT ET AL) 9 June 1998 (1998-06-09) column 13, line 21 - line 29; claims ---	1-22
A	US 4 758 654 A (BROD WILLIAM B ET AL) 19 July 1988 (1988-07-19) claims -----	1-22

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internal Application No

PCT/US 00/07573

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9639450 A	12-12-1996	US 5672666 A	30-09-1997
		AU 700247 B	24-12-1998
		AU 5952196 A	24-12-1996
		BR 9609361 A	18-05-1999
		CA 2219856 A	12-12-1996
		EP 0830393 A	25-03-1998
		JP 11504972 T	11-05-1999
WO 9732905 A	12-09-1997	NO 960898 A	08-09-1997
		AU 1948497 A	22-09-1997
		CN 1212709 A	31-03-1999
		EP 0885247 A	23-12-1998
US 5442019 A	15-08-1995	CA 2186400 A	05-10-1995
		CN 1157000 A	13-08-1997
		DE 69501888 D	30-04-1998
		DE 69501888 T	12-11-1998
		EP 0751965 A	08-01-1997
		ES 2118585 T	16-09-1998
		JP 2858957 B	17-02-1999
		JP 9511006 T	04-11-1997
		WO 9526370 A	05-10-1995
		US 5753786 A	19-05-1998
		US 5672665 A	30-09-1997
		US 5747612 A	05-05-1998
DE 4241530 A	16-06-1994	AT 403921 B	25-06-1998
		AT 206493 A	15-11-1997
US 5763543 A	09-06-1998	AU 3587495 A	29-03-1996
		AU 694803 B	30-07-1998
		AU 3587995 A	29-03-1996
		CA 2198776 A	21-03-1996
		CA 2199869 A	21-03-1996
		CN 1167493 A	10-12-1997
		EP 0781301 A	02-07-1997
		EP 0781300 A	02-07-1997
		JP 10506659 T	30-06-1998
		JP 10506418 T	23-06-1998
		WO 9608521 A	21-03-1996
		WO 9608520 A	21-03-1996
		US 5712352 A	27-01-1998
US 4758654 A	19-07-1988	EP 0339122 A	02-11-1989
		CA 1300311 A	05-05-1992
		CN 1022251 B	29-09-1993
		JP 1026608 A	27-01-1989
		JP 1984905 C	25-10-1995
		JP 7005661 B	25-01-1995
		KR 9304758 B	05-06-1993
		AT 68504 T	15-11-1991
		GR 3003573 T	16-03-1993

